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## PATENT SPECIFICATION

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### COMPLETE SPECIFICATION

#### Alloy Steel Printing Plates

I, CLEMENTS BATCHELLER, citizen of the United States of America, of 7, Pearl Street, Glens Falls, in the State of New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

My invention relates to the art of printing and particularly to a new type of metal printing plate or master and to the method of producing the same.

A large proportion of all the general printing done in the United States is done by photolithography in which a printing master, consisting of a zinc or aluminium plate bearing a developed photo image, is employed. These metal plates have practically entirely superseded lithographic stones.

Zinc and aluminium are comparatively soft, coarse-grained metals, and while press plates prepared therefrom work fairly satisfactorily in slow operating, flat bed, offset-printing presses, these plates are often damaged and frequently break down completely under the heavy roll impact of the modern rotary presses. In the printing of multi-color jobs requiring the use of several printing masters it is not uncommon for zinc and aluminium plates to show damage or develop printing imperfections after a relatively few printed copies have been struck off. Surface defects, due to cracks, checks, slivers and slag particles in the soft base metal, frequently develop, and irregularities, resulting from poor graining, such as a partial loss of sensitivity or failure of the photo image to adhere properly to the surface of the printing master, cause the plates to gum up in the one case and result in partial loss of the image in the other.

In the initial preparation of a printing master the surface of the zinc or aluminium plate is subjected to a "graining" treatment to enable it to hold a uniform water or moisture film thereof. This is a necessary prerequisite of any plate which is to be used as a printing master. The graining of zinc or aluminium sheets is an operation entirely

separate from their manufacture and is usually done by firms which make a business of supplying the printer with suitably grained plates for his purposes. Graining, by the methods now employed, is a purely mechanical operation and consists in making the plate to be grained the bottom of a box in which are placed an abrasive and a number of marbles made of steel, carborundum, porcelain, glass or wood; the coarseness of the abrasive and the size of the marbles depending on the coarseness of the grain required. The assembly is placed in an oscillating machine and the balls are rolled over the surface of the sheet until the desired roughness has been attained.

The serious defects inherent in these soft metals have been recognised and attempts have been made to substitute stainless steels therefor. Resistance to corrosion is an important factor because both the grained plates and the printing masters are usually stored for some time, and therefore stainless steels, because of their greater hardness and inherent resistance to corrosion would be superior to plates of zinc or aluminium. Another serious defect of both zinc and aluminium plates is their tendency to surface oxidize almost instantly in the presence of even slight atmospheric moisture. Such oxide surface films seriously impair the affinity of the plate for lithographing ink.

So far as I am aware, however, stainless steels have not been successfully employed to any appreciable extent in printing masters because of the difficulties involved in graining the steel by the usual methods. Stainless steels and particularly those of the 18-8 type, containing about 18% of chromium and 8% nickel, by weight, are hardened by cold working. For this reason the ball graining hardens the metal and leaves the plate in a distorted condition which prevents its proper application to the press. In my particular case, however, the property of increasing hardness of the metal under continual use, serves in an important degree in prolonging the working life of the plate which actually becomes better under prolonged printing use. This is just the

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reverse of the soft metal plates.

As stated above, one of the essential characteristics of any material which is to be used as a printing master is that it must be capable of holding on its surface a uniform film of moisture. Another factor affecting the life of the plate and the quality of the printing that can be done with it, is its ability to hold intact the image imparted thereto. In the present types of zinc and aluminium plates this image holding ability is dependent almost entirely on adhesion because these plates have little or no absorptive properties. On the other hand, plates prepared according to my process are capable of absorbing to a considerable degree the light sensitive film applied thereto so that the developed image does not merely adhere superficially to the plate but is deeply imbedded therein. Turpentine, which is used in printing from such plates, when applied as a thin film to my colored plates, is entirely taken up to surface dryness in a few minutes. The same applies to a film of light petroleum oil.

My invention therefore consists in the provision of an improved printing master comprising a plate of chromium containing alloy steel provided on the printing face thereof, with a grain formed by electrolytic etching and having an image forming substance superposed on predetermined zones of said face.

The invention also includes a lithographic printing plate formed of stainless steel, the printing surface of said plate having integral therewith metal granules formed by electrolytic etching and of a size and uniformity of distribution adapting said surface for fine photo-lithographic printing, a slightly absorbent colored film comprising oxides of the elements in said steel integral with said granules, and an image forming substance superposed on predetermined zones of said film.

In addition my invention includes the method of making a photo-lithographic printing plate formed of stainless steel which comprises graining the surface of said plate by subjecting it to electrolytic action as anode at a current density sufficient to effect a micro etching of the surface thereof and in an electrolyte containing a plurality of ingredients of which the following are the only necessary ingredients:—sulphuric acid, a second acid selected from the group consisting of chromic, vanadic, metavanadic, manganic, and permanganic, and the balance substantially water, whereby distortion of said plate is avoided, and thereafter applying an image forming substance to 60 predetermined zones of said surface.

As pointed out above, one of the insurmountable difficulties heretofore encountered in the preparation of corrosion-resistant alloy steel sheets or strips for use in printing masters is that of producing a suitable grained surface on the sheet or strip and, at the same time, maintaining it in a true plane. I find that a surface grain particularly adapted for use in the making of a printing plate can be formed on the surface of a chromium-containing alloy steel by my electrolytic treatment. By such treatment, the surface is not only grained but, as distinguished from the surface produced by mechanical means, is rendered very passive against subsequent corrosion. In other words, my treatment simultaneously produces an oxidized surface having a grain effect therein in the form of an electric etch extending uniformly over the entire surface of the sheet (both front and back) and which is highly resistant to corrosion. Such a surface, without my further treatment, is capable of holding a uniform moisture film for a period as long or longer than a mechanically grained plate of zinc or aluminium.

I prefer to use stainless steels of the chromium-nickel type, such as 18—8, because the results attained with nickel-containing steels are superior to those attained with the straight chromium steels. However, it is to be understood that any steel containing chromium in substantial quantities, say over 5% or 6% by weight, may be used and that the term "stainless steel" as used throughout this application includes such steels. Since the treatment is confined to the surface of the steel. Its gauge or thickness is not of material importance except from a cost standpoint. It may be said however, that stainless steel strips in "paper thin" gauges, say of the order of about 0.0095" in thickness, are entirely suitable and are much better adapted for use in rotary press applications than the thicker gauges. Moreover, in thicknesses of this order the number of square feet per pound of metal is very large and the cost per unit of area is correspondingly small.

In the treatment of the metal I prefer to use an electrolyte formed by mixing together—

	Parts by weight
Water	900
Sulphuric acid (1.84 sp. gr.)	330
Sodium bichromate	180

The steel is immersed in this bath and electrolytically treated as anode by passing direct current therethrough for a period of about ten to thirty minutes at a current density of about one to two

amperes per square inch of anode, considering the area of one side only of the anode. As a cathode I prefer to use a tellurium lead sheet of any reasonable dimensions and I find that its position in relation to the anode is of little importance due to the very heavy throwing power of the electrolyte. Both surfaces of the anode are microscopically etched substantially irrespective of the size or position of the cathode. The electrolyte is preferably used at normal room temperature, say from 60° to 70° F. although at higher temperatures, say from 100° to 135° F. the processing time is considerably reduced. Higher current densities up to 2½ amperes per square inch may be used not only to hasten the process but also to increase the roughness of the plate surface. That is to say, within reasonable limits, the higher the current density, the faster the micro-etching will take place, the larger the surface grains will be, and the greater will be the surface metal losses.

Another formula which may be used is as follows:

	Parts by weight
Water	200
Sulphuric acid (1.84 sp. gr.)	180
Sodium bichromate	50

The sodium bichromate in either case reacts with the sulphuric acid to produce chromic acid and sodium sulphate. Thus, 1% of sodium dichromate will yield in the solution about 0.67% of chromic acid and will consume about 3.28% of sulphuric acid. During this reaction there will also be formed in the solution about 1.09% by weight of hydrated sodium sulphate.

While I prefer to use sodium bichromate, I find that any of the chromates or dichromates, or straight chromic acid, may be used.

Instead of any of the chromates or dichromates, I may use vanadic acid, metavanadic acid, or any of the vanadates of metavanadates of ammonium, potassium or sodium. The addition of any of these vanadates or meta vanadates to the sulphuric acid solution forms therein vanadic or metavanadic acid together with a sulphate of the vanadate or metavanadate-forming element, just as in the case of the use of chromate or dichromates the sulphate or bisulphate of the chromate or dichromate-forming element is produced.

Although less satisfactory, any of the manganates or permanganates of the alkali metals of Group I, the manganates or permanganates of the alkaline earth metals of Group II, or manganes dioxide, may also be employed with the sulphuric acid. These manganates and

permanganates form manganic or permanganic acid by reaction with the sulphuric acid.

The quantity of free sulphuric acid in the solution as finally formed is of course somewhat less than that in the initial sulphuric acid-water solution. Generally speaking, an electrolyte which will show upon analysis the following ingredients within about the proportions set forth may be used.

	Per cent by weight	
Water	35-55	
Free Sulphuric acid (1.84 sp. gr.)	15-55	80
Chromic, vanadic, metavanadic, manganic or permanganic acid	2-20	
Sulphates or bisulphates and impurities	Balance	85

The grained surface produced by the foregoing treatment on chrome-nickel stainless steels is a brilliant silver white which I consider an important feature in my invention.

Instead of graining my plates entirely by electrolytic etching it is possible to grain them partially by mud blasting and then to complete the graining by treating them electrolytically as described above. By blasting the surface with highly liquid sludge of fine abrasive grit under comparatively low pressure, no appreciable work hardening or distortion of the plate will occur. After the blasting, the surface of the plate will be a dull-gray color and quite susceptible to corrosive attack. But by then subjecting the plate to electrolytic action as described above, to complete the graining, the dull gray surface will be converted into one of extreme whiteness and brilliancy, and the original stainless characteristics of the surface will be restored.

In the selection of steel having a proper mill finish for graining by my process, a 2B finish, i.e. a bright cold rolled finish is recommended. In the rolling of stainless steels into thin gauges, certain annealing operations are necessary which form upon the surface of the steel a semivisible oxide film which is smooth in texture but slightly porous. A 2B finish is not only cheapest finish commonly applied to stainless steels, but the porous characteristics of the oxide surface film on stainless steels having this finish make it peculiarly suitable for my use.

I find it preferable so to treat the steel in the micro-etching or graining step that this oxide film is not entirely removed. If the steel is not anodically treated as above described for not more than about ten to

15 fifteen minutes at a current density of about 0.5 ampere per square inch of total surface a good proportion of this film will remain intact although the color thereof, in the case of chrome-nickel steels, will become a brilliant silvery white.

10 Without any further treatment, my plates, at this stage, may be processed by any master plate maker for use in photolithography. Their ability to hold the developed image upon the plate under the steps of "work up", inking, and sensitizing and desensitizing will be found equal in all respects to zinc or aluminium plates but they will have a much longer working life due to the use of the harder and tougher metal.

20 However, further treatment of my grained plates in the manner hereinafter described will produce a printing master far superior to those formed of zinc or aluminium. By further processing the grained plates it is possible to form integral with the surface thereof a color film composed of hydrated oxides of the metals in the plates themselves. These films are extremely thin but somewhat porous and thereby substantially increase the absorptive properties of the surface.

30 The hydrated oxides of the elements in the steel can be developed in the colored surface film by merely immersing the grained plates in any of the foregoing solutions, but without the application of an electric current thereto, although I prefer to use the specific solution made according to the second mentioned formula above and at a temperature of from 180° to 220° C. At lower temperatures the time required to develop the hydrated oxides is greatly prolonged and at higher temperatures the results are not as satisfactory.

45 Due to the silvery white surface produced by the anodic treatment of the steel and the translucency of the oxide film formed in the second step of my process, the color of the film, which is ordinarily black on steels with any ordinary mill finish, is here of less intensity than black. Thus, after from 20 to 30 minutes treatment at a temperature of say 185° F., an olive green film may be developed, and if the treatment is prolonged beyond the time of formation of the green film the color changes to a light maroon. The fact that these colors are sufficiently light to offer a sharp contrast with the lithographing ink employed is an important feature of my invention because it permits the printer, by inspection from time to time during printing operations, easily to determine the character of the printing image.

65 The matter of image retention on the

printing master and its integrity has always been troublesome to lithograph printers using masters of zinc or aluminium because, in such case, the retention of the image is merely a matter of its adhesion to the surface of the plate. As distinguished from an image which merely adheres to the surface of the plate, the images, or rather the image forming substances, on my plate are actually absorbed to a considerable degree by the oxide films. Since this film is in and integral with the steel and is not a mere surface coating, the image on my masters may very well be said to be integral with the steel.

Printing masters have been made from my plates merely by hand transfer methods directly from a lithographic stone. For example, an old lithograph stone in stock for thirty years was cleaned up and re-inked by a master printer and an ink impression taken therefrom by means of a transfer paper. This impression was imparted to one of my stock plates by merely placing the inked paper in direct contact with the surface of the plate and transferring the impression by rolling. Upon removing the paper it was noted that the ink image had been completely and perfectly taken up by the prepared surface of my oxide colored plate due to its high absorptive properties.

After drying, the plate was placed on the press and subjected to the usual procedure to sensitize and desensitize certain portions of it preparatory to inking up and printing therefrom. Prolonged printing runs from this printing master showed great superiority over plates of zinc and aluminium in the clarity of the printing, the ability of the plate to remain absolutely free from "gumming up" and its perfect retention of the image due to its deep penetration into the oxide films in the plate surface.

While I prefer to use a current density of about one ampere per square inch of area of one side only of the anode (0.5 ampere per square inch of the total anode area) because this current density produces an excellent fine grain with a low metal loss, it is to be understood that somewhat lower and considerably higher current densities may be employed. Generally speaking, the coarseness of the grain produced and the loss of metal from the anode all vary directly, while the time required for the processing varies inversely with the current density employed.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A printing master comprising a plate of chromium-containing alloy steel provided on the printing face thereof with a grain formed by electrolytic etching and  
5 having an image forming substance superposed on predetermined zones of said face.
2. A lithographic printing plate formed of stainless steel, the printing surface of said plate having integral therewith metal  
10 granules formed by electrolytic etching and of a size and uniformity of distribution adapting said surface for fine photolithographic printing, a slightly absorbent colored film comprising oxides of the  
15 elements in said steel integral with said granules, and an image forming substance superposed on predetermined zones of said film.
3. A printing master comprising a plate  
20 of stainless steel grained by electrolytic etching and having integral with the printing surface thereof a slightly absorbent colored film comprising oxides of iron and chromium; said surface being  
25 capable of retaining a substantially uniform film of moisture thereon, and predetermined zones of said colored film being impregnated with an image forming substance.
4. A lithographic printing plate formed of a chromium containing alloy steel and having a printing surface thereon comprising metal granules integral with said  
30 plate of a size and uniformity of distribution adapting it for fine photo-lithographic printing and produced by treating said surface electrolytically as anode, whereby  
35 distortion due to mechanical graining is avoided, said surface having an image forming substance superposed on predetermined  
40 zones thereof.
5. A printing master or plate as set forth in any claims 1 to 4, in which the original material is of chrome-nickel stainless steel, for example of the 18-8 type.
6. The method of making a photo-lithographic printing plate formed of stainless steel which comprises graining the surface of said plate by subjecting it to electrolytic action as anode at a current density  
50 sufficient to effect a micro etching of the surface thereof and in an electrolyte containing a plurality of ingredients of which the following are the only necessary ingredients:—sulphuric acid, a second acid selected from the group consisting of  
55 chromic, vanadic, metavanadic, manganic and permanganic, and the balance substantially water, whereby distortion of said plate is avoided, and thereafter applying an image forming substance to predetermined zones of said surface.
7. The method of making a photolithographic printing plate as set forth in claim 6, including the step carried out prior to the application of the image forming  
65 substance, of forming a color film of slightly absorbent oxide on said grained surface by immersing the plate for a period and without the passage of current in a film forming bath containing the electrolyte defined in claim 6.
8. The method of making a photolithographic printing plate as set forth in claim 7, in which the film-forming bath is maintained at a temperature of from  
75 about 180° to 220° F.
9. The method of making a photolithographic printing plate as set forth in any of Claims 6 to 8, in which the electrolyte contains, by weight, from about 15%  
80 to about 55% of sulphuric acid and from about 2% to about 20% of the second acid.
10. The method of making a photolithographic printing plate as set forth in any claims 6 to 9, in which the current  
85 density employed in the anodic treatment is from about 1 to 2.5 amperes per square inch of surface to be grained.
11. The methods of making a photolithographic printing plate as set out in  
90 the preceding specification.
12. Photo-lithographic printing plates when made by any of the methods of claims 6 to 11.

Dated the 11th day of June, 1945.

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